PRODUCTION AND PHYSICAL METALLURGY

OF PURE METALS -- PART VIII

- USSR -

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Self-Diffusion of Molybdenum and Diffusion of
Tungsten in Molybdenum

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Ye. V. Borisov, P. L. Gruzin, L. V. Pavlinov
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edeniye Chistykh Metallov (Production and
Physical Metallurgy of Pure Metals), No. 1,
Moscow, 1959, pages 213-218.7

Molybdenum is a refractory metal melting at 2620°.
This property of molybdenum combined with its high strength
maintained during heating to high temperatures permits its
use in parts for electrovacuum instruments and electron
tubes. Molybdenum and its alloys are easily oxidized in
air at temperatures above 600° and therefore need special
protection against oxidation.

High mechanical properties at elevated temperatures
depend on the strength of the interatomic bonds in the
crystal lattice, which is characterized by the activation
energy of self-diffusion /1/. The knowledge of diffusiom
characteristics permits the determination of atomic mobility
at different temperatures, an important factor due to which
molybdenum maintains its strength at elevated temperatures.
It is known that diffusion processes determine recrystalization,
sintering, weakening of metals and alloys, and many other
processes.

The study of diffusion in molybdenum has certain
specific features related to the high melting point of
molybdenum. Considering that the majority of methods for
determination of the diffusion coefficient have a lower
limit of sensitivity on the order of 10^{-13} cm^2/sec, the
minimum temperature of diffusion annealing of molybdenum
must be above 1500°. Therefore, a vacuum furnace with a
tungsten heater was used for diffusion annealing. Annealing

was carried out under the continuous action of three vacuum and diffusion pumps so that the air pressure in the furnace was on the order of 10^{-4} mm Hg.

The investigation of diffusion was carried out in the range of 1800 to 2175°. The duration of annealing was between a few hours and a few tens of hours. The temperature was regulated by an autotransformer. Molybdenum prepared by arc melting under vacuum was used for the tests. The specimens were subjected to prior annealing at 1500° for 20 hours in an atmosphere of hydrogen. The chemical analysis showed the presence of 0.7% of tungsten in molybdenum. Other admixtures were slight.

Radioactive isotopes of molybdenum and tungsten Mo^{99} and W^{185}, were used for the tests. They have a half-life of 67 hours and 73 days, respectively. Diffusion coefficients were determined by the method of measuring the total radioactivity of the remaining specimen /2/. Radioactive isotopes were deposited electrolytically in a thin layer on the specimens. Radioactivity was measured with a radiometric counter instrument.

The results of measurements of the self-diffusion coefficient of molybdenum and the diffusion coefficient for tungsten in molybdenum vs temperature are shown in Figs. 1 and 2, respectively. These data satisfy the equations:

$$D = 4 \, exp \, (-115\,000/RT) \ cм^2 \cdot sec^{-1}$$

for self-diffusion in molybdenum, and

$$D = 5 \cdot 10^{-4} \, exp \, (-78\,000/RT) \ cм^2 \cdot sec^{-1}$$

for tungsten diffusion in Molybdenum.

Definite relationships between the diffusion characteristics and the heat resistance of the alloys have been shown in a number of works /3/, /5/. The upper temperature limits of the usefulness of alloys and certain other factors are determined by the rate of diffusion of elements composing the alloy. Solid solutions with high heat resistance are those that have low diffusion coefficients. Among metals a special place is occupied by molybdenum, which differs from metals of the iron group in its uniquely low level of diffusion mobility (Fig. 3).

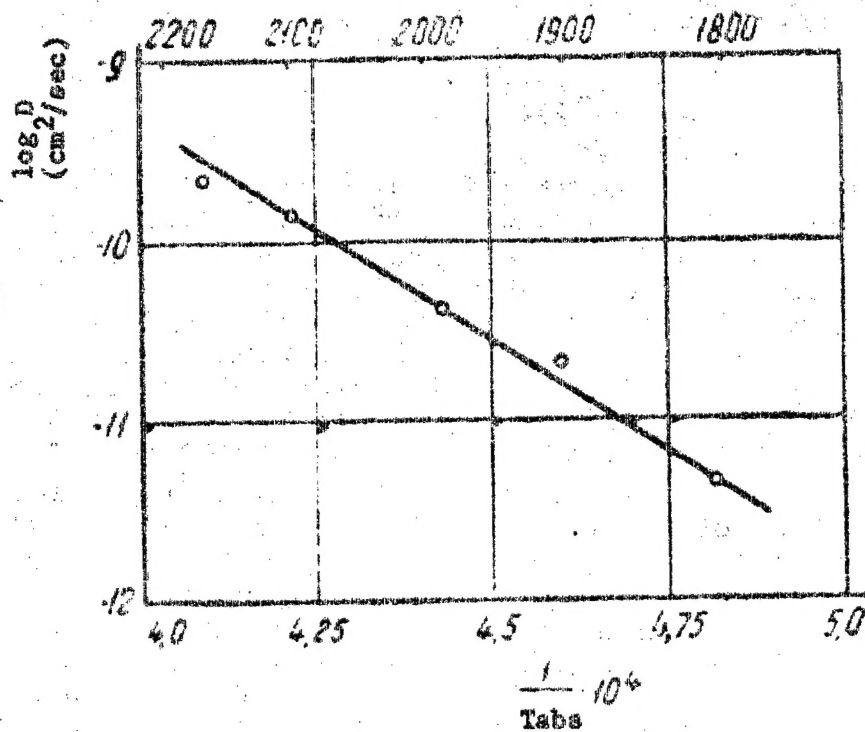From the table it appears that the self-diffusion coefficient of molybdenum is lower than the self-

Fig. 1. Self-diffusion coefficients of
melted molybdenum vs temperature.

diffusion coefficients of nickel and cobalt factors of 10^{11} at $700°C$, by 10^8 at $1000°C$ and 10^3 at $1300°C$.

In article /4/ it was shown that recrystallization of many metals takes place at approximately the level of diffusion mobility characterized by self-diffusion coefficients of the order of 10^{-22} cm^2 sec^{-1}. Data on self-diffusion of molybdenum confirm this premise. Indeed, at the temperature of recrystallization, which is approximately $880°$, self-diffusion coefficients of molybdenum are of the above magnitude.

Thus, data on self-diffusion of such refractory metals as molybdenum confirm the existence of a threshold level of diffusion mobility or recrystallization of pure metals.

It is shown that the alloying of metals not only shifts the temperature of recrystallization but also the level of diffusion mobility at which recrystallization becomes possible. The upper limit of diffusion mobility in solid solutions can reach 10^{-13} cm^2 sec^{-1} /4/. The threshold level of diffusion mobility for recrystallization in solid solution also determines whether the alloys have high strength at elevated temperatures. It very definitely determines the fact that, in the area of working temperatures of refractory alloys, self-diffusion coefficients of pure metals and diffusion coefficients of alloying elements composing the base of the alloy are about 10^{-13} to 10^{-14} cm^2 sec^{-1} /4/, /5/. The limiting diffusion mobility for recrystallization of solid solution ($D = 10^{-13}$ cm^2 sec^{-1}) is also the limiting diffusion mobility for intensive weakening of alloys previously strengthened by plastic deformation or by dispersion hardening. Consequently, using data on self-diffusion of molybdenum and keeping in mind the threshold levels for recrystallization and for weakening of solid solutions, one can tentatively evaluate the upper limit of the temperature range of recrystallization and weakening of molybdenum solid solutions. According to our study, this temperature is of the order of $1600°C$. Thus, this temperature determines the potential heat-resistance level of alloys based on molybdenum. This temperature range can be achieved by alloying with elements that do not substantially change the level of diffusion mobility and the strength of interatomic bonds. According to literature data, the temperature of molybdenum recrystallization is substantially increased by alloying with titanium, zirconium and niobium /6/, although it does not reach its limit figure. One can show that in this case Q and D_o of self-diffusion decrease, although by a relatively
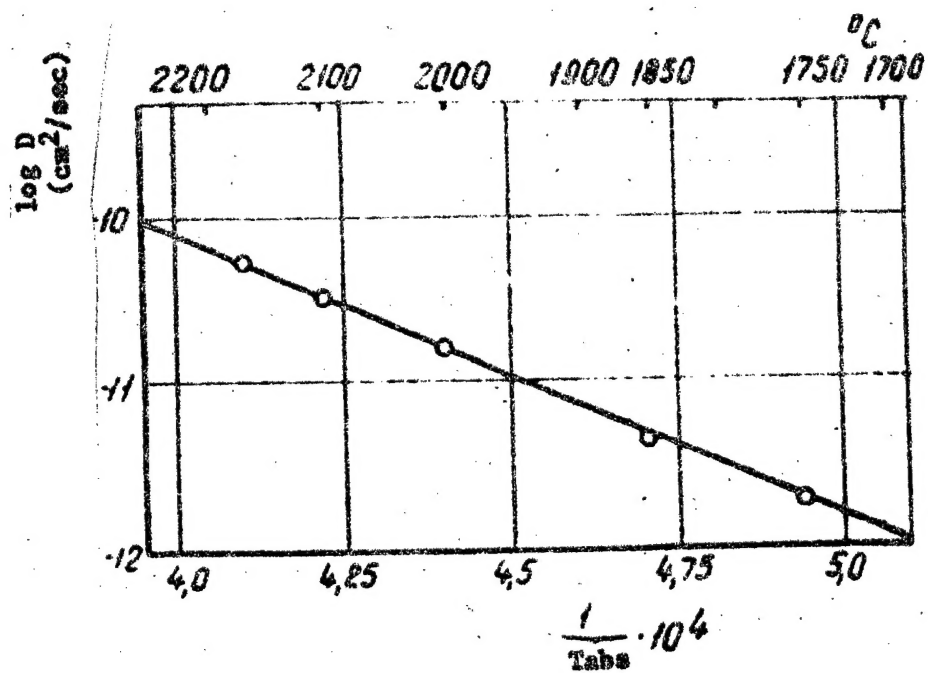
Fig. 2. Diffusion coefficient of tungsten in melted molybdenum vs temperature.

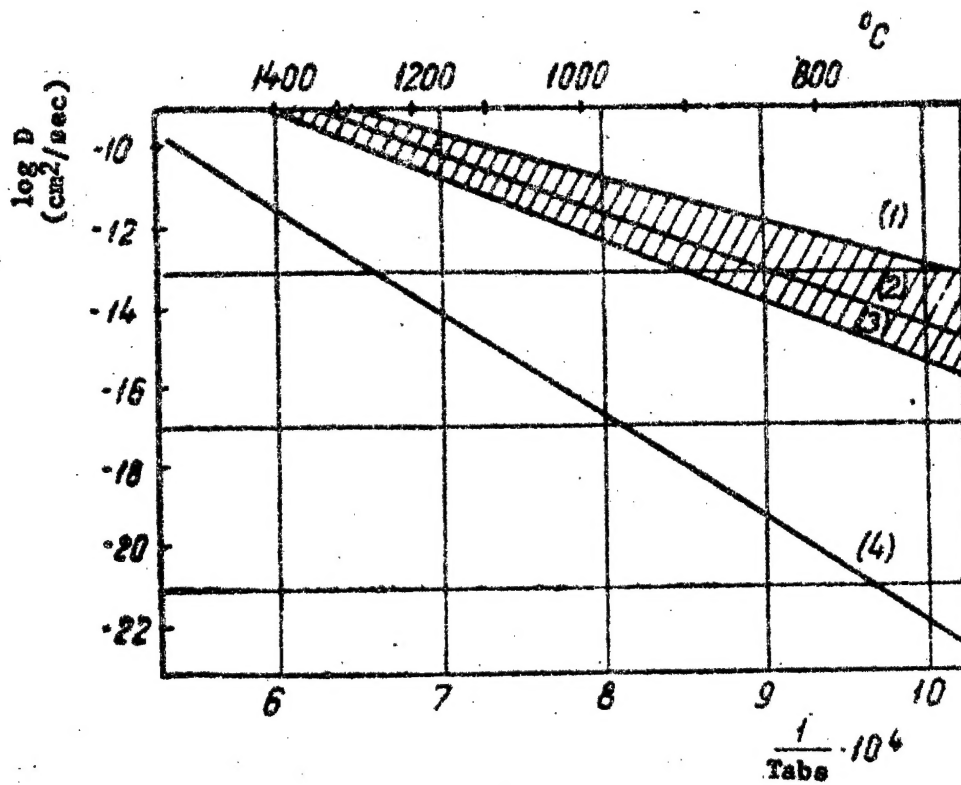Fig. 3. Self-diffusion coefficients of nickel (1), cobalt (2), iron (3) and molybdenum (4) vs temperature.

Table 1

Coefficients of Metal Self-diffusion

Metals	D, cm^2 sec^{-1}			
	700 C	1000 C	1200 C	1400 C
Nickel	10	10	10	
Cobalt	10	10	10	
Y-Iron		10	10	
Molybdenum	10	10	10	10^{-1}

small quantity which however, determines the deviation of the actual recrystallization temperature from the limit.

The magnitude of the activation energy of self-diffusion observed in such refractory metals as molybdenum satisfies the relation $Q = 40 T_s$, where Q is the activation energy of self-diffusion and T_s is the melting point /7/. Actually, according to the data of our study, $Q/T_s = 39.6$. Data on molybdenum confirm the assumption regarding the relationship between activation energy and sublimation heat. The sublimation energy for molybdenum S is 160,000 cal/g-atom /8/. The ratio Q/S is 0.72, i.e., the activation energy of Mo self-diffusion is approximately 2/3 of its sublimation energy.

Recently it was hypthesized that in body-centered metals, diffusion can occur through rotation of a ring composed of four atoms /9/. Based on such diffusion mechanics, calculations for molybdenum self-diffusion /10/ result in $D = 16 \exp (-120,000/RT)$ cm^2 sec^{-1}. As shown here, theoretical parameters of molybdenum self-diffusion agree with experimental data. As could be expected, the activation energy of heterodiffusion (tungsten in molybdenum) is lower than the activation energy of molybdenum self-diffusion (78,000 and 115,000 cal/g-atom, respectively).

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Diffusion in High-Temperature Alloys on a Cobalt Base +

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i Metallovedeniye Chistykh Metallov (Production
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Moscow, 1959, pages 219-223./

Cobalt alloys are used in high-temperature and high-pressure technology. It is interesting to study the diffusion of different elements in cobalt alloys to ascertain the role of the diffusion process in weakening refractory alloys at high temperatures.

The deformable cobalt-chromium-tungsten-molybdenum alloy VK36 was used as the object of investigation. Carbides constitute the strengthening phase of this alloy. The development of carbides, due to a diffusion shift of basic and second-phase atoms, results in a strengthening of the alloy. Therefore, the present work concerns the diffusion of elements in the alloy base (cobalt) as well as in the strengthening phase (chromium and tungsten). The influence of carbon and molybdenum on diffusion constants was studied. For this purpose an alloy with a minimum content of carbon (0.025%) as well as a similar alloy without molybdenum were prepared. The chemical composition of the alloys investigated is given in Table 1.

After being melted, the alloys were subjected to preliminary pressing for the destruction of dendrite structure. This was followed by a homogenizing anneal in hydrogen at 1100° for 50 hours. The billets were then forged into rectangular rods with cross sections of approximately 40 X 15 mm from which samples 30 X 10 X 8 mm were prepared.

Prior to diffusion annealing, one side of each specimen was coated with a thin layer of a radioactive element (Co^{60}, Cr^{51}, W^{185}). Cobalt and chromium were coated electrolytically, tungsten by electric spark. Further, the specimens were screwed together in pairs with their active sides in contact and were placed in evacuated quartz tubes. Diffusion annealing was carried out in tubular furnaces at temperatures ranging from 850 to 1250°. Diffusion coefficients were determined by measuring the integral radioactivity of the remaining part of the specimen after elimin-

+) The work was carried out in 1950-52. The basic results were submitted to the AS USSR and MIFI (Moscow Institute of Physical Engineers)

Table 1

Alloys	C	Si	Mn	Ni	Cr	S	P	Al	Fe	Mo	W	Co
VK-36	0,21	0,15	0,07	21,96	20,13	0,003	0,003		1,38	5,00	5,00	Base
VK-36-S	0,025	0,39	0,13	19,58	18,50	0,010	0,005	0,37	2,77	5,1	4,58	Base
VK-36-S-Mo	0,03	0,28	0,19	20,86	20,00	0,006	0,002	0,2	0,44	—	5,00	Base

ation of successive layers /1/.

The study of cobalt self-diffusion in the alloys investigated showed that the addition of carbon somewhat decreases the activation energy and increases the self-diffusion coefficients (Fig. 1 and Table 2). A similar influence of carbon was disclosed during a study of iron self-diffusion in steel, as was mentioned in article /2/ and later confirmed /3/.

The results obtained show that the addition of molybdenum increases the activation energy and decreases the self-diffusion coefficients of cobalt. This effect of molybdenum was observed many times in connection with other types of alloys.

Investigation of the diffusion of chromium, which enters into the VK36 alloy in the amount of 20%, is also of considerable interest. Besides the fact that chromium enters in the composition of the solid solution of the basic alloy, it is a strong carbide-forming element and therefore it participates in the strengthening phase. It is evident that this enhanced tendency toward carbide formation causes the activation energy of chromium diffusion to be highest in an alloy with maximum carbon content. Thus, the presence of carbon in these alloys somewhat increases the activation energy and decreases the chromium diffusion coefficients (Fig. 2 and Table 2). It is interesting to note that a similar influence of carbon on chromium diffusion was detected in article /4/, in which it was shown that an increase in carbon content in the refractory alloy ZhS-3 increases the energy of activation by about 0.1% /sic/ -- from 76 to 82 kcal/g-atom -- and decreases the diffusion coefficients.

The different influence of carbon on cobalt and chromium diffusion indicates the different character of the interaction of these diffused elements with carbon atoms in the solid solution.

The retarding of chromium diffusion is apparently a substantial factor in improving refractory properties of the VK36 alloy. In Fig. 2 the straight dotted line shows the temperature dependence of the chromium diffusion coefficient in the KhN80T alloy /5/. The corresponding straight line for the VK36 alloy runs nearly parallel to the former but lower. The character of the distribution of these straight lines can be observed also for another strong carbide-former, tungsten (Fig. 3) In this case the diffusion coefficients of the VK36 alloys are lower than corresponding coefficients the KhN80T alloy by nearly half an order.
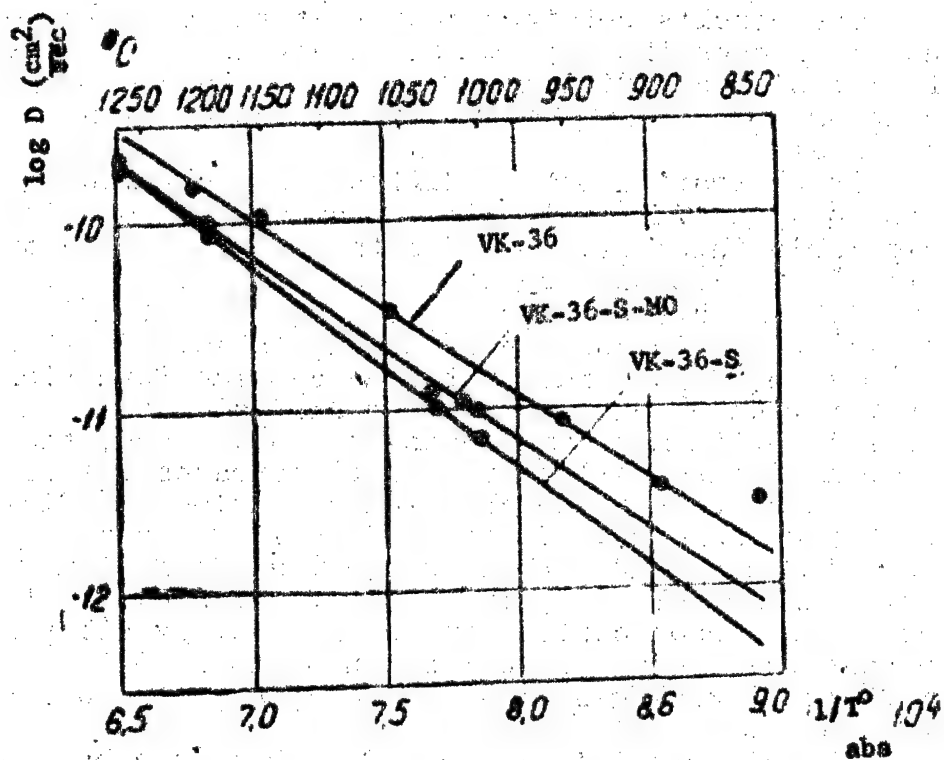
The addition of molybdenum to the base of the VK36

Fig. 1. Self-diffusion coefficient of
cobalt in alloys vs temperature.

Table 2

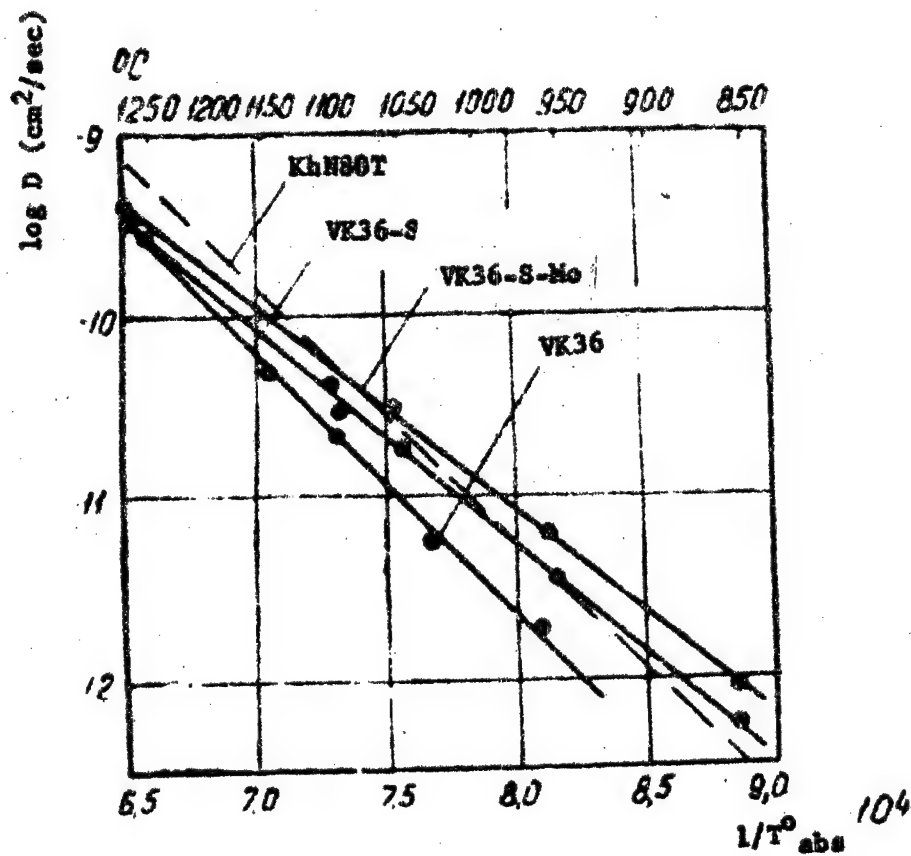| Diffusing Element	Alloy	D_0 cm2/sec	Q cal/g-atom
Co	VK-36	$9\cdot10^{-4}$	46 000
	VK-36-s	$3\cdot10^{-3}$	50 000
	VK-36-s-Mo	$5\cdot10^{-4}$	45 000
Cr	VK36	3	69 000
	VK-36-s	$3\cdot10^{-2}$	56 000
	VK-36-s-Mo	$8\cdot10^{-1}$	51 000
	KhN80T	2	66 000
W	VK36	$1\cdot10^{-3}$	51 000
	KhN80T	$1.5\cdot10^{-3}$	48 000

Fig. 2. Diffusion coefficients of chromium
in alloys vs temperature.

Table 3

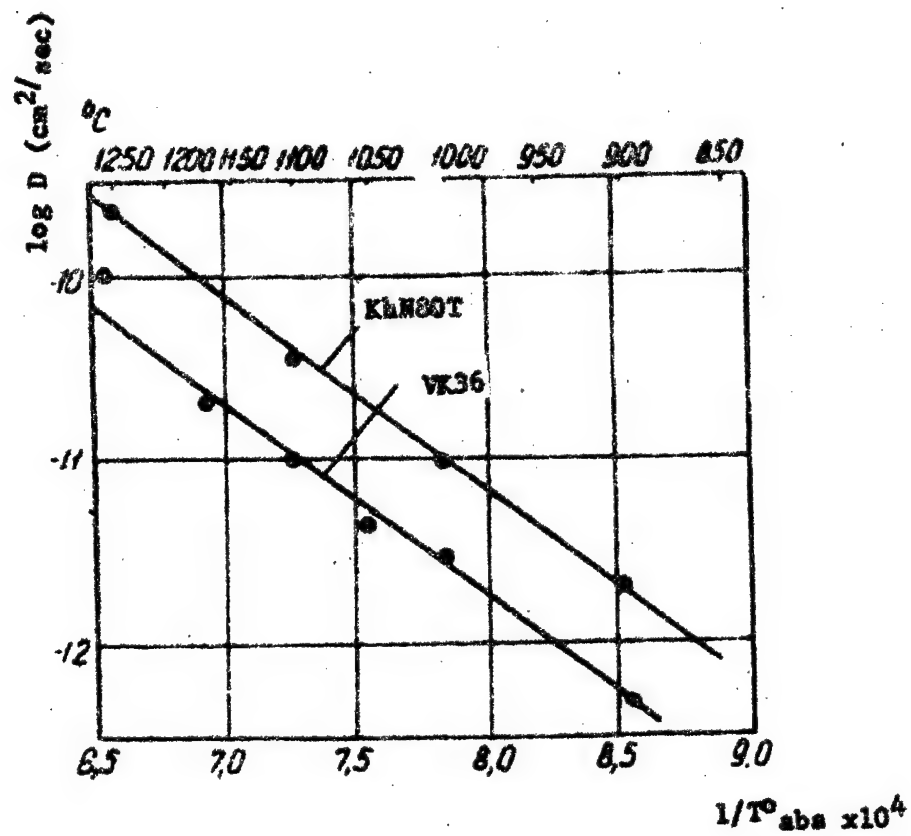| Diffusing element	D_o VK36-S-Mo	Q, VK36-S-Mo	D_o, VK36-S	Q, VK36-S
Co	$1.7 \cdot 10^{-}$			0.9
Cr	$2.7 \cdot 10^{-}$			0.91

Fig. 3.   Diffusion coefficients of tungsten
          in alloys vs temperature.

alloy influences the diffusion of chromium in the same way as it does the diffusion of cobalt. Table 3 compares the ratios of the pre-exponential factors and activation energies of VK36-C and VK36-S-Mo alloys for cobalt and chromium diffusion. The practical coincidence of these figures signifies that the addition of molybdenum to VK36-type alloys changes the diffusion parameters of cobalt and chromium in the same way. This also confirms in the conclusion concerning the beneficial action of molybdenum on the diffusion in the refractory VK36 alloy.

The results of the investigation of diffusion in alloys based on cobalt confirmed a conclusion drawn by us earlier regarding the correlation of diffusion characteristics with heat resistance, as obtained for alloys of the KhN80T type. In particular, in the area of working temperatures, the threshold level of diffusion mobilities for cobalt alloys as well as for Kh80T-type alloys is characterized by diffusion coefficients on the order of 10^{-12} to 10^{-13} cm^2/sec.

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Changes in Physical Properties During Decomposition of the β-Phase in an Alloy of Zirconium with 15% Niobium

Some works have indicated confirmation of the possibility of strengthening by aging /since/ zirconium alloys have a cubic β-solid solution structure after hardening from the β-range.

Litton /1/ found that an alloy of zirconium with tantalum (17.5%), after hardening from 1000°C, in water and aging for 2 hours at 500°C, has a high tensile strength equal 97.2 kg/mm^2, which is higher by 20 kg/mm^2 than the tensile strength of rolled alloys of similar composition. We have observed an increase in hardness of zirconium alloys with niobium after annealing at 300 and 500°C /2/. As a result of 8 hours of annealing at 300°C, the hardness of hardened alloys with 6-20% niobium had increased on the average by 50 Brinell units.

Depending on the duration of annealing at 480°C, the hardness of a zirconium alloy with 5.5% molybdenum increases during the first 15-30 minutes from 300 to a maximum of 450 Vickers units whereas, during further aging it gradually decreases, returning to its initial value after 100-200 hours /3/.

By comparing these results with studies of aging of titanium alloys, and after radiographic investigation of hardened and annealed alloys, the authors of article /3/ arrived at the conclusion that in the course of the dissociation of an alloy with 5.5% molybdenum a transitional phase is formed which is analogous to the ω-phase of titanium alloys.

The changes in physical properties during the aging of zirconium alloys have not been studied and there are no data in the literature concerning the properties of the transitional phase. The study of the influence of the transitional phase on the physical properties of the alloys(with the aid of the thermophysical method) is required for plotting state diagrams for finding the strongest zirconium alloys.

We have studied the changes of a number of physical properties of alloys with cubic β-phase structure during heating to 900°C and subsequent cooling. A Zr Alloy with

15% Nb was used in the study of aging processes in connection with the dissociation of the metastable β-phase. This alloy was selected for study because it contained the minimum quantity of niobium (15%) at which the cubic -phase is formed. In alloys with a lower content of niobium, the -phase is partially dissociated even when hardening is done in water, whereas in alloys with a higher content of niobium, dissociation is much slower and its effect is less. After hardening, the alloy has the greatest electrical resistivity (100 microhms/cm) and the smallest elasticity modulus (5,200 kg/mm^2) of all zirconium alloys with niobium /4/.

When hardened from 600°C and higher, the alloy has a β-solid solution structure, whereas at temperatures below 560° it undergoes eutechtoid dissociation into an α-phase and a β-solid solution containing 93% niobium.

Preparation of Specimens and Methods of Measuring Physical Properties

Alloys were prepared in an MIFI-9-3 arc furnace having a copper sole and tungsten electrode, in an atmosphere of chemically pure argon purified by melting a zirconium getter rod. The arc was powered by a welding generator with a 10 kw rating and was ignited by touching the electrode to a tungsten rod pressed into the furnace sole.

Ingots weighing about 70 g were cast in a cavity of the copper sole and formed in rods about 90 mm long.

After hot forging at 800-600°C, the alloys were cleaned of scale, sealed in quartz ampoules and hardened in water after 4 hours of aging at 1,100°C. Cylindrical specimens 4 mm in diameter and approximately 85 mm long were prepared from the hardened billets. The surfaces of the specimens were polished. These specimens, when heated to 900°C, were used for measuring normal elasticity modulus, specific electrical resistivity and thermal expansion. Specimens 15 mm in diameter were taken from the same ingot for the measurement of hardness after annealing at different temperatures.

The elasticity modulus of the alloy was determined according to the specimen's resonant frequency when bent in the vacuum installation as described in article /4/. The specific electrical resistivity was measured with double Thomson bridge in a vacuum installation (10^{-4} mm Hg). Potentiometer leads were made of thick molybdenum wire. A good contact of the leads with the specimen was maintained by spring clamps during heating.

Thermal expansion of the alloy was studied on a vacuum dilatometer. An indicator-gage with a dial with

0.001 mm divisions was used for measuring elongation. This permitted determination of the changes in specimen size during the transformations.

Hardness during heating was determined on an installation by M. G. Lozinsky. The size of the imprints produced on the slides when the samples were under pressure from a diamond pyramid with a load of 1 kg was determined by means of a microscope. The heating of the specimen during the measurement of its physical properties was carried out at a rate of 5°C per minute.

The annealing of specimens was effected in 30 minutes, and hardened specimens were charged in a hot furnace. The density of the alloys was determined with the use of a pyknometer. After annealing, the hardness was determined with a Rockwell device and converted into Brinell units.

Experimental Results and Discussion

As noted before, the alloy hardened in water from 1100°C has high specific electroresistivity (100 microhms/cm) and low elasticity modulus (5200 kg/mm^2), which indicates great distortion of the crystal lattice of the alloy.

Upon heating to 350°C, the elasticity modulus of the alloy declines somewhat, and at higher temperatures it increases to 7200 kg/mm^2, i.e., to a value far greater than the elasticity of same alloy the β-solid solution state. The dependence of elasticity modulus (see Fig. 1) on the heating temperature can be considered as a monotonically decreasing curve on which is imposed a maximum peak of the elasticity modulus at 520°C. The modulus show a monotonic increase as the alloy is cooled, beginning at 900°C and reaching 5950 kg/mm^2 at room temperature. No peaks were observed during cooling. The only explanation of the abrupt increase in elasticity modulus upon heating, to values exceeding the elasticity modulus of the alloys in β-solid solution state or after slow cooling, is the formation of a new phase with a high elasticity modulus the dissolution of the hardened β-solid solution. Under continuous heating, the new phase is formed in the range of 350-520°C, the maximum quantity being present at 520°C. On heating above 520°C, the quantity of the new phase decreases. The alloy annealed for 30 minutes at 350°C had an elasticity modulus of 9000 kg/mm^2, i.e., a higher one than after uninterrupted heating.

The data show that the elasticity modulus of this transition phase is very high.

According to the results of dilatometric studies, the dissociation of the β-solid solution and the formation

of the transition phase begin at 300°C and cease at 470°C, which results in a decreased coefficient of linear expansion over this temperature range, i.e., the new phase has a smaller specific volume than the β-phase of same composition. Heating above 470°C results in the dessociation of ω-phase and the formation of α-phase, accompanied by an 0.52% increase in volume.

Judging from the dilatometric curve, the specific weight of the alloy after cooling is less than that in the β-solid solution state, which corresponds to the results of specific weight measurements.

The hardened alloy had a density of 6.938 g/cm^3, and after annealing at 520°C and cooling, the density was 6.895 g/cm^3.

Specific electrical resistivity of the hardened alloy decreases from 100 to 96 microhms/cm during heating to 300°. A negative temperature coefficient of resistivity is unusual for metals and in this case is probably a consequence of the decreasing distortion of the crystal lattice in the β-solid solution.

The peak of the curve of specific resistivity, 109 microhms/cm at 500°, is the result of the high-resistivity transition phase formed in the range of 350-500°C.

In the range of 500-700°C, the quantity of the new phase decreases. The increase of resistivity upon heating above 700° is the consequence of the normal increase in electrical resistivity of alloys with temperature. It must be noted that upon cooling of the alloy, no anomalies in the variation of electric resistivity with temperature are observed; the decrease is monotonic down to 83 microhms/cm. This is due to the fact that the transitional phase disappears upon heating above a certain temperature and, judging by thermophysical curves, it does not reappear upon subsequent cooling. It is possible that the transitional phase can be formed also during cooling in the range of 600-300°C, i.e., in a range of minimum stability of the β-solid solution.

The Vickers hardness of cast alloys declines monotonically during heating to 400°C from 450 to 275 units, while in the range of 400-600°C a peak with a maximum of 325 units is observed at 500° due to the formation of the transitional phase. It was observed that imprints taken in the range of transitional phase formation are uneven, which shows the complexity of the structure and the brittleness of the transitional phase.

It is interesting that during the formation of the transitional phase both the elasticity modulus and the hardness increase, i.e., both the strength and the forces of interatomic bonding in the alloy increase.
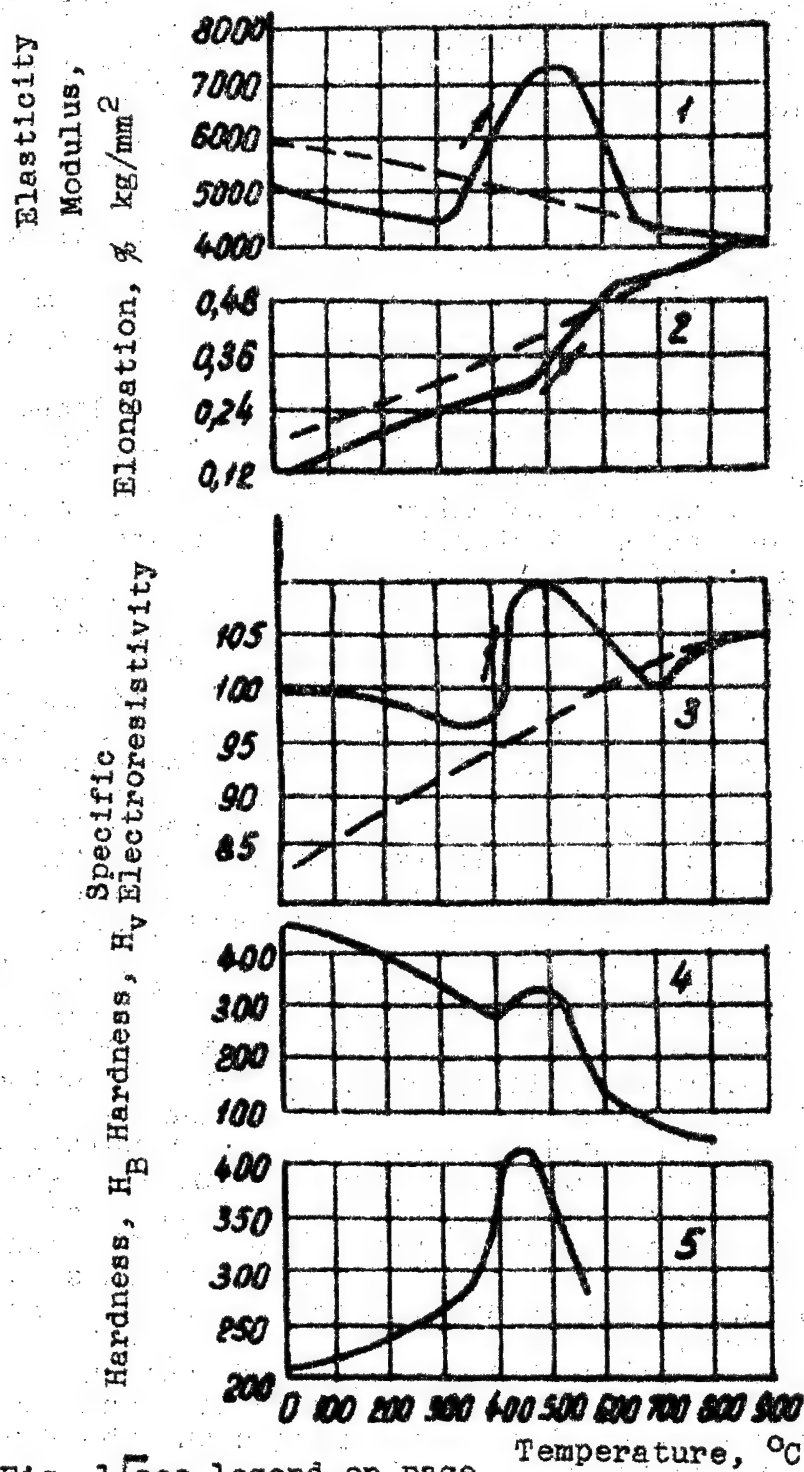
Fig. 1 [see legend on page 23]

Fig. 1 [continued from preceding page]
Elasticity modulus (1), elongation
(2), specific electrical resistivity
(3), hardness in Vickers units (H_v)
(4) vs temperature of zirconium
alloy with 15% niobium hardened from
β-solid solution at the rate of 5°C
per minute. Brinell hardness (H_B)
of hardened alloy after annealing at
different temperature for 30 minutes.

The application of different methods to the study of dissociation is interesting in that such properties as electrical resistivity and elasticity modulus depend on the composition of the solid solution and on the state of the dissociation but depend only slightly on the discharges, while the hardness depends very much on the presence of dispersed discharges. All methods result in data confirming the formation of the transition phase on dissolution above 300°C.

To clarify the question of the relation between the results of the study of β-solid solution dissociation under continuous heating at a rate of about 300°C per hour and the changes in properties during the isothermal dissociation of the β-phase, the hardness of the alloy was measured after 30 minutes of isothermal annealing at temperatures of 200 to 550°C. It was found that maximum hardness, equal to 400 Brinell units (corresponding to a tensile strength of 100 kg/mm^2) is observed after annealing at 420 to 470°C, whereas after uninterrupted heating, the maximum electrical resistivity, hardness, and elasticity modulus are observed at 500°C, i.e., at a slightly higher temperature.

Increased hardness of the alloy is observed even after isothermal annealing at 220°C.

A zirconium alloy with 20% niobium also showed increases in elasticity modulus and in hardness (from 190 Vickers units to a maximum of 290 units at 500°C), in the case of continuous heating of the alloy hardened from β-solid solution.

The particular properties of the ω-phase combined with heat treatment permits the preparation of zirconium-based alloys with high elasticity and strength. After annealing at 480°C an alloy with 15% niobium, a hardness of 400 Brinell units was obtained, whereas after annealing at 350°C, the elasticity modulus of the alloy was 9000 kg/mm^2, i.e., the values of the properties were nearly doubled.

Conclusion

The process of dissociation of the stable β-phase under continuous heating at a rate of about 5°C per minute and with isothermal annealing was studied for a zirconium alloy with 15% niobium hardened from β-solid solution.

During the heating, the dissociation of the β-phase passes through a transition phase in the range of 350-500°C which is accompanied by considerable increaes in elasticity modulus, hardness and specific electrical resistivity, and a decrease of the linear expansion coefficient.

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Effect of Alloying on Young's Modulus of Zirconium

It is important to know the elastic properties of
an alloy, both with regard to its use in specific structural
applications and under certain working conditions, and for
the study of the interactions of metals in the process of
alloying. When preparing alloys for use at high temperatures,
zirconium alloys in particular, it is necessary to study the
dependence of the elastic modulus on the temperature.

Only scant data concerning the elastic properties of
zirconium alloys are given in the literature. It is known
that Young's modulus for zirconium free of hafnium, as
measured by dynamic methods, is 10,270 kg/mm^2 /1/. The
elastic modulus of Zircalloy-2 (an alloy of zirconium with
1.5% tin and small additions of iron, nickel and chromium)
is equal to 9,800 kg/mm^2 at room temperature and 6,465 kg/mm^2 at 500°C /2/. The elastic modulus of an alloy with
2.5% tin is equal to 9,800 and 5,600 kg/mm^2 respectively, at
the above temperatures /3/.

We have studied the influence of different alloying
elements on Young's modulus for zirconium at temperatures
of 20 to 1,000°C. The following alloys were selected for
the study:

(1) Zirconium, with elements fairly soluble in
α-zirconium (oxygen, aluminum, tin, and titanium);

(2) Zirconium, alloyed with elements that produce
cubic β-structure at room temperature when hardened from
the β-range (niobium, molybdenum, tantalum);

(3) Zirconium, with elements forming intermetallic
phases (silicon, slightly soluble in α-and β-zirconium, and
aluminum introduced into the alloy in quantities above its
solubility limit).

Preparation of Alloys

Iodide zirconium, 99.7% pure and containing 1.1%
hafnium, was used as the base for these alloys. Alloys with
oxygen were prepared by melting zirconium with zirconium
dioxide. To prepare alloys with titanium, TG-0 titanium

sponge was used. Other alloying elements were of chemically pure grade.

The melting was done in an MIFI -9-3 arc furnace on a copper water-cooled sole using a nonexpendable tungsten electrode in an atmosphere of chemically pure argon, which was purified by melting a zirconium getter. The arc was fed from a welding generator rated at 10 kw, and the current in the arc exceeded 400 amps. The arc was ignited by touching a tungsten electrode pressed into the sole of the furnace, so as to avoid contamination of the ingots by tungsten.

After repeated remelting, samples were cast into a special cavity of the copper sole. The rods cast had a length of 90 mm and diameter of about 12 mm. The weight of the castings was 65 tc 70 g.

All alloys, except those with 10% tin, 5% aluminum and 3% silicon by weight, were forged in air at 600-950°C to a size of 8-10 mm. The forging process was brief and the alloys did not become deeply oxidized. After forging, the ingots were cleaned of scale and annealed in quartz ampoules.

Alloys with 0.2 and 0.5% oxygen, 5% tin, and 3% aluminum by weight were annealed at 900°C; those with 2 and 10% tin and 2% aluminum by weight at 850°C; and those with 1, 2 and 3% silicon by weight at 800°C. The annealing period was 72 hours, after which the alloys were quenched in water.

Alloys with molybdenum, niobium and tantalum were kept in the β-range at 1200°C in quartz ampoules filled with argon at a pressure up to 200 mm Hg for 6 hours, and then were hardened in water.

After further heat treatment, specimens 3-4 mm in diameter were prepared and 80-95 mm long, and the surfaces were polished.

The moduli of elasticity of these specimens were measured, and the hardness, specific electric resistivity and microstructure were studied.

Methods of Study

The elastic moduli of the alloys were calculated according to the resonance frequency of freely suspended curved cylindrical rod specimens.

Each specimen was suspended on two thin molybdenum wires, one of which was attached to the membrane of a telephone and the other to a piezoelectric oscillation adapter-receiver. The vibrator and the receiver were secured inside a vacuum chamber suspended by vacuum rubber. Electrical oscillations were imposed on the vibrator by a

ZG-10 oscillator. Determination of the resonance frequency of the specimen was effected on an electronic ZO-4 oscillograph.

Melting of the specimen was carried out in a furnace with molybdenum-heaters and with a slot for suspension of the specimen.

A few measurements of each sample were taken at heating and cooling rates of 7-8°C per minute. The methods of measuring the elastic modulus is described in more detail in the articles /4/ and /5/.

Elastic Modulus of α-Solid Solutions

From the state diagram /6/ it is known that at 800°C zirconium forms an α-solid solution with tin (up to 5 wt-%) aluminum (up to 1-2 wt-%) oxygen (up to 10-12 wt-%), whereas at 500°C zirconium forms an α-solid solution with titanium (up to 100 wt-%). Of these four elements, oxygen, aluminum and tin increase the temperature of the $\alpha \to \beta$ transformation, whereas the temperature of the $\alpha \to \beta$ transformation in alloys with titanium shows a minimum with 33 wt-% titanium.

The alloys of zirconium with titanium are of special interest for the study of elastic properties, inasmuch as these elements form a continuous series of solid solutions in both the α-and β-ranges. In zirconium alloys with titanium, annealed at 500°C, the minimum elastic modulus observed was 8,170 kg/mm^2, with a content of about 33 wt-% (50 atom-%) titanium (Fig. 1). The same composition shows a minimum temperature of 545°C for $\alpha \to \beta$ transformation, i.e., the minimum stability of α-solid solution during heating occurs at 545°C /6/. For alloys with titanium quenched in water from the β-range, the elastic modulus has values only slightly different from those shown in Fig. 1, such that in pure zirconium the β-phase in zirconium alloys with titanium is scarcely fixed even by rapid quenching in water.

Changes in the elastic modulus of zirconium alloyed with elements raising the temperature of the $\alpha \to \beta$ transformation were studied in samples with oxygen (up to 0.5 wt-%) tin (up to 10 wt-%) and aluminum (up to 3 wt-%) annealed in the α-range. The results of measurements are shown in Table 1, which also contains data concerning the hardness and electrical resistivity of the alloy. Changes in the elastic modulus with the composition of alloys with tin, aluminum, and silicon are shown in Fig. 2 in atom-%.

Alloying with 2% tin resulted in a decrease of the elasticity modulus from 10,800 to 9,500 kg/mm^2; additions of larger quantities of tin (up to 10 wt-%) resulted in an additional, though small, decrease of the above figure to
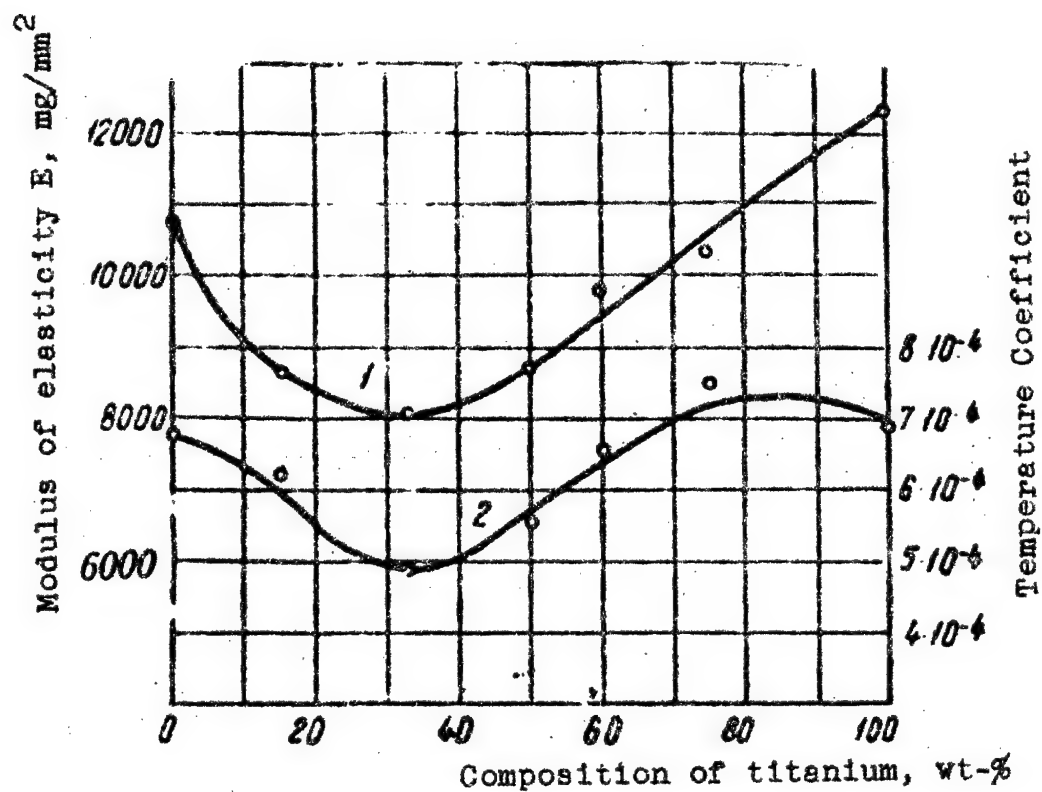
Fig. 1. Elastic modulus (1), and its
temperature coefficient in the range
range of 20-500°C (2), for
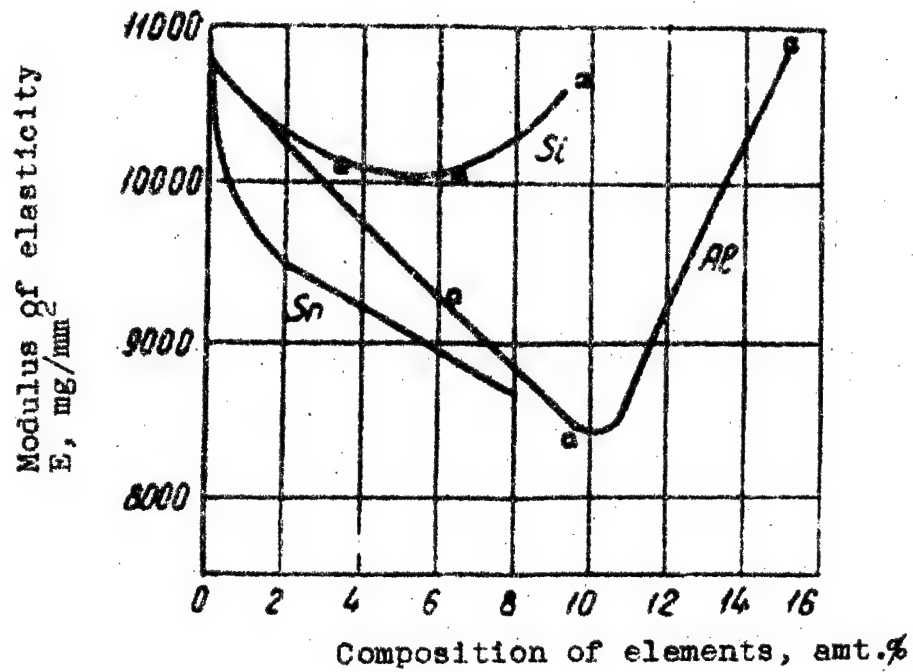zirconium alloyed with titanium.

Fig. 2. Dependence of elastic modulus
on the composition of alloys
of zirconium with aluminum,
silicon, and tin.

Table 1

Moduli of normal elasticity of zirconium alloys at room temperature

Alloying Element	Weight, %	Atom-%	Annealing temp., °C	Elastic modulus	Specific electrical resistivity microhms, /cm	Brinell hardness converted from R_B to R_C
Tin	2,0	1,54	850	9550	72	120
	5,0	3,88	900	9280	121	-
	10,0	7,88	850	8730	144	187
Aluminum	2,0	6,46	850	9190	141	217
	3,0	9,46	900	8370	158	212
	5,0	15,08		10900	87	288
Oxygen	0,2	1,13	900	9745	61	158
	0,5	2,78	900	9895	73	253
O + N (getter)	-	-	800	9200	-	-
Titanium	15,0	25	500	8590	79	225
	33,0	48,6	500	8170	94	280
	50,0	65,5	500	8530	97	280
	60,0	74	500	9700	90	250
	75,0	85	500	10330	78	225
	100	100	500	12200	-	-
Tantalum	25,0	14,4	1200	8500	-	-
	25,0	14,4	750	9350	53	189
Molybdenum	10,0	9,55	1200	6780	102	-
Silicon	1,0	3,44	800	10070	52	136
	2,0	6,65	800	10010	-	-
	3,0	9,745	800	10600	67	193

8,700 kg/mm^2.

The addition to zirconium of w wt-% aluminum decreased the elastic modulus to 9,190, whereas the addition of 3% aluminum decreased it to 8,370 kg/mm^2. Oxygen addition (0.2 and 0.5 wt-%) also decreased the elastic modulus to 9,700-9,900 kg/mm^2. For zirconium contaminated by nitrogen and oxygen (the sample prepared from the getter), the elasticity modulus was found to be 9,200 kg/mm^2.

Thus it was established that the elastic modulus of unalloyed iodide zirconium at room temperature is higher than the elastic modulus of α-solid solutions formed by different elements on a zirconium base.

In the range of α- solid solutions, the elastic modulus decreases monotonically with increase of the alloying elements. It is probable that this is due to an increased distortion of the lattice of the α-solid solution with addition of the alloying elements.

Investigation of -Solid Solution Alloys

The elastic moduli of zirconium alloys of cubic β-phase structure, i.e., alloys with niobium, tantalum and molybdenum, were studied (Table 1). In alloys containing more than 15% niobium, the β-phase is fully fixed when the alloy is hardened from the β-region. In alloys with a lower content of niobium, the β-phase partially dissociates upon hardening. In an alloy with 10% molybdenum, a considerable quantity of β-phase was fixed after hardening.

Zirconium alloys with niobium, hardened from the β-range, have lower values of elastic modulus than zirconium; an alloy with 15% niobium (Fig. 3) showed the minimum value, 5,200 kg/mm^2. This alloy having a minimum quantity of niobium when hardened from the β-range alloys as a cubic solid solution. At a lower content of niobium, the β-phase partially dissociates during hardening. The same composition shows maximum electrical resistivity.

The investigation proved that alloying that forms β-solid solutions results in an elastic modulus that decreases more rapidly with temperature than does that of a solid solution based on α-zirconium.

Zirconium-based alloys with α-solid solution structure and a hexagonal, densely packed lattice showed no such low elastic moduli as were observed for alloys with body-centered cubic structure. Zirconium alloys with up to 100 wt-% titanium in the α-phase were found to have a minimum elastic modulus of 3,100 kg/mm^2 (Fig. 1), whereas among alloys with niobium hardened from the β-range and to a body-centered cubic structure the minimum elastic modulus

was 5,200 kg/mm^2 (Fig. 3). This is a result of the metal-stability of the supercooled β-phase.

Dissociation of Hardened β-phase

In certain alloys of zirconium the metastable β-phase with a body-centered cubic lattice fixed by hardening has a low elastic modulus. In zirconium alloys with 10 wt-% molybdenum hardened from water at 1200°, the elastic modulus was seen to decrease slightly, whereas in the range of 325-450°C, it increased considerably (by 600 kg/mm^2), up to values higher than the elastic modulus at room temperature (Fig. 4). These changes take place because of the dissociation of the hardened β-phase. The dissociation of the β-phase begins at a noticeable rate upon heating above 325°C, i.e., at relatively low temperatures. When a previously cooled alloy was heated no increase in elastic modulus was observed, owing to the fact that, during slow cooling, a partial dissociation of the metastable β-phase takes place. The increase of elastic modulus was also observed upon heating hardened Zr-25% Ta alloys. The fact that the elastic modulus of hardened Zr-10% Mo alloy rises to higher values upon heating in the range of 325-450°C or after slow cooling together with the furnace (Fig. 4) can be explained by the formation of a transitional phase with a high elastic modulus and a complex structure. This formation takes place during the transition from the supercooled β-phase to a stable structure. When cooled with the furnace, the transitional metastable phase apparently dissociates. An analogous transitional ω-phase in alloys based on titanium has been studied in detail /7/.

The elastic modulus of an alloy with 25% tantalum annealed at 750°C is higher than the elastic modulus of the same alloy hardened from 1200°C, owing to the dissociation of the β-phase and its transformation into a mixture of stable phases (Table 1). A similar situation was observed for zirconium alloys with niobium (Fig. 3).

Elastic Modulus of Alloys Containing Intermetallic Phases

The elastic modulus of a pure intermetallic compound is difficult to measure, owing to the brittleness of the compound. Among the alloys with intermetallic phases in their structure, we studied alloys with 5 wt-% aluminum and with 1, 2 and 3 wt-% silicon.

It is known from literature data /6/ that silicon is only very slightly soluble in zirconium (less than 0.2% at
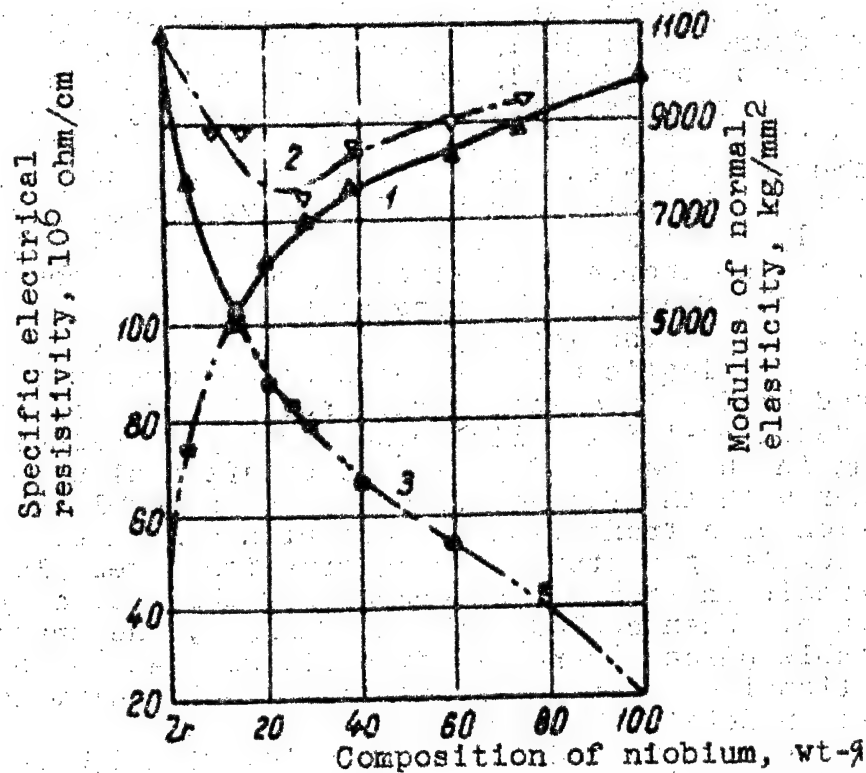
Fig. 3. Elastic modulus and
specific electrical
resistivity of hardened
zirconium alloys with
niobium: 1- alloys hardened
in water from 1100°C; 2 -
alloys annealed for 80 hours
at 525°C; 3 - specific
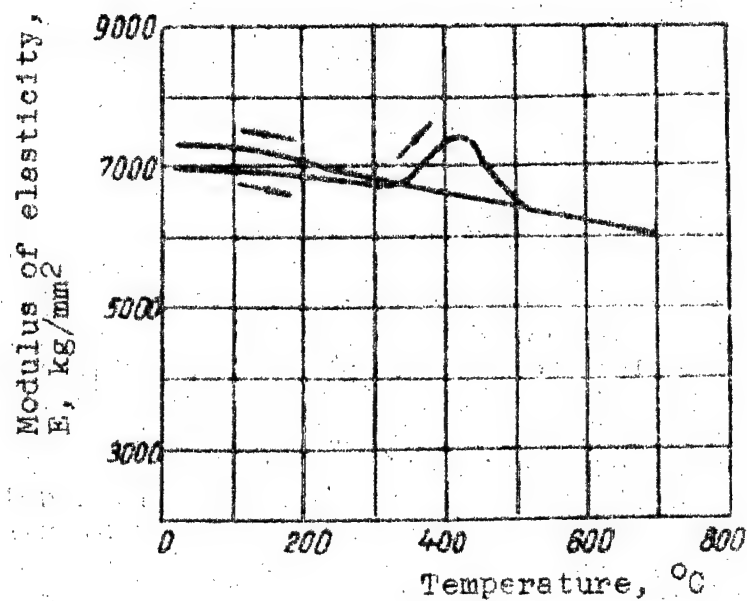electrical resistivity.

Fig. 4. Changes in elastic modulus
during heating of water-quenched,
hardened Zr-10% Mo alloys.

all temperatures up to 1600°C). This is confirmed by the slightness of the changes in the electrical resistivity of zirconium when it is alloyed with 1 to 3% silicon (Table 1). The compound nearest to zirconium, Zr_2S_1, contains 7.14 wt-% silicon; it is an intermediate phase in the system with Zr_3Al containing 8.8% aluminum, the maximum solubility of aluminum in zirconium being 3.5% at 940°C.

Alloying zirconium with 1 wt-% (3.4 atom-%) silicon resulted in a slight decrease of the elastic modulus to 10,000 kg/mm^2, whereas introduction of 3 wt-% (9.7 atom-%) silicon increased the elastic modulus at room temperature to its value for unalloyed zirconium (Fig. 2). A further increase in the content of the compound $\overline{/Zr_2S_1\overline{/}}$ in the alloy would probably result in a further increase in the elastic modulus. Alloying zirconium with 1-3% of slightly soluble silicon changes the elastic modulus of zirconium to a considerably lesser extent than does alloying it with elements that form solid solutions based on zirconium.

From Fig. 2, one sees that alloying zirconium with a considerable quantity of aluminum (5 wt-%, 15 atom-%) raises the elastic modulus to 10,900 kg/mm^2, which is much greater than the elastic modulus for smaller additions of aluminum and forms alloys with the α-solid solution structure. This is due to the presence of a considerable quantity of intermetallic phase in the alloy containing 5% aluminum. Alloys containing intermetallic phases have high elastic moduli, exceeding by far the elastic moduli of zirconium at high temperatures (Fig. 5) probably because the elastic properties of intermetallic phases change less with temperature.

The elastic modulus in the solid-solution range decreases with an increase of aluminum content, but when an intermetallic structure is formed it increases considerably (Fig. 2).

Influence of Temperature on the Elastic Modulus of Alloys

Determination of the elasticity moduli of alloys during heating yields data concerning elastic properties of different structural components vs temperature, and also data concerning processes taking place in the alloys.

The elastic moduli of zirconium alloys with elements forming α-solid solutions are lower than those of zirconium, not only at room temperature but at higher temperatures also. At 500°C, the elastic moduli with 15 and 33 wt-% titanium are lower by 1600 kg/mm^2 than those of zirconium at the same temperature; moduli for the alloys with 0.2 wt-% oxygen and
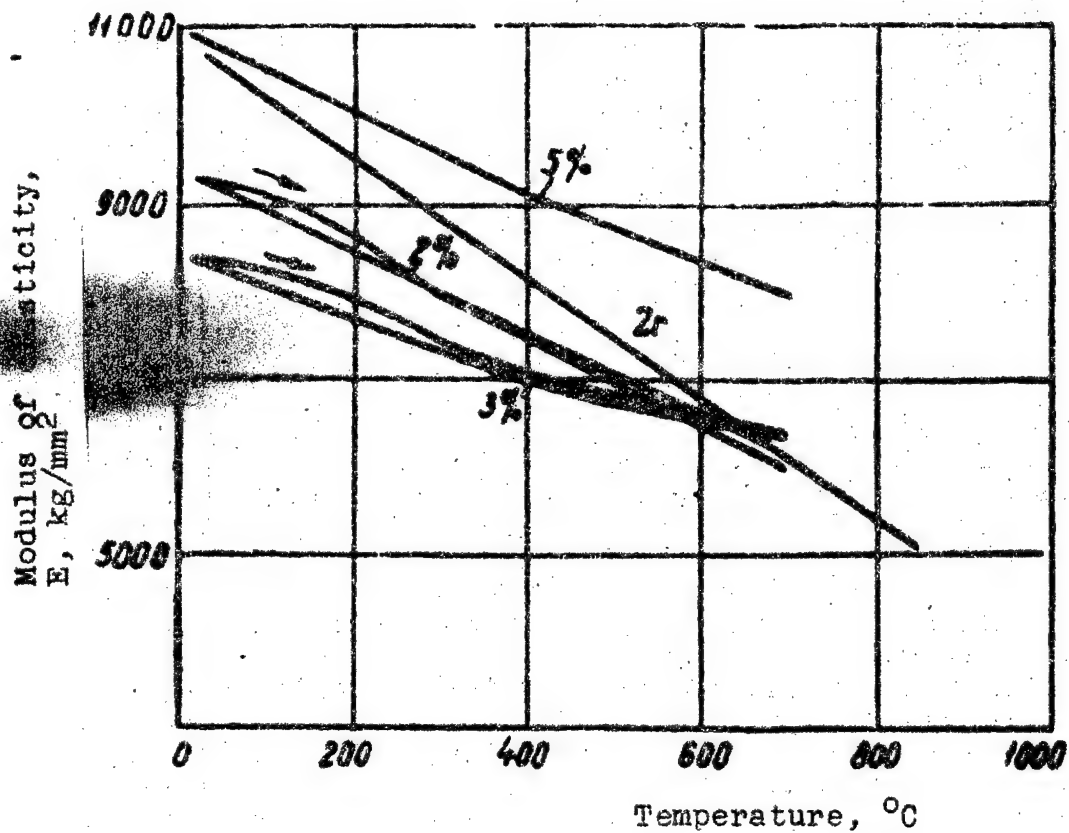
Fig. 5. Changes in elastic modulus of zirconium
alloys with 2, 3 and 5 wt-% aluminum
during heating and cooling.

2 to 10 wt-% tin are lower by 800 and 1300 kg/mm² respective-
ly. If this content is increased to 10%, the elastic modulus
increases, but, at the same time, its rate of decrease with
the temperature becomes smaller (Table 2). The result is
that at about 800-900°C the elastic moduli of alloys with
2-10% tin are comparable with the elastic moduli of zirconium,
but lower than the latter at 800°C.

The elastic moduli for all alloys of zirconium with
titanium at any temperature up to 1000°C.

The curves of the elastic modulus of zirconium alloyed
with titanium, vs composition, at temperatures below the
$\alpha \longrightarrow \beta$ transformation, show minima; however, the minima be-
come less pronounced with increase of temperature to 500°C,
provided the alloy with minimum elastic modulus also has the
minimum modulus temperature coefficient (Fig. 1).

Zirconium alloys with 2 and 3 wt-% aluminum have
lower elastic moduli than zirconium at room temperature,
whereas at 600°, their elastic moduli are equal to 6,500
kg/mm², i.e., they approach the elastic modulus of zirconium,
(Fig. 5). The alloy with 5% aluminum, containing about 57%
intermetallic Zr$_3$Al (8.80 wt-% aluminum), has a high elastic
modulus at room temperature, considerably higher than that
of zirconium at elevated temperatures (Fig. 5). The 3 wt-%
silicon alloy with considerable intermetallic phase in its
structure (about 40%) has a higher elastic modulus at ele-
vated temperatures than an alloy with 1% silicon or pure
zirconium (Fig. 6).

The greater the quantity of intermetallic phase in an
alloy, the higher the elasticity modulus and the lower the
temperature coefficient of the modulus, owing to the fact
that the strength and other elastic properties of inter-
metallic compounds depend less on the temperature than do
the same properties of pure metals and ductile alloys. For
α-solid solutions, the difference between the elastic moduli
of the alloys and of zirconium decreases with rising tempera-
ture and approaches zero, whereas in zirconium alloys con-
taining intermetallic phases, the difference in elastic
modulus increases with increasing temperature.

In alloys with silicon, thermoelastic methods have
shown that the transformation into cubic β-phase occurs at
810-860°C (Fig. 6).

In unalloyed zirconium and also in alloys with titanium
and tin, a decrease in elastic modulus by about 700-1000
kg/mm² was observed upon heating owing to a transformation of
the densely hexagonal packed α-lattice into a body-centered
cubic β-lattice of lower modulus. In an alloy with 10% tin,
the transformation was observed at higher temperatures than
in an alloy with 2% tin, which concurs with the zirconium-tin

Table 2

Temperature Coefficient of Elastic Modulus
of Zirconium Alloys (20-700°)

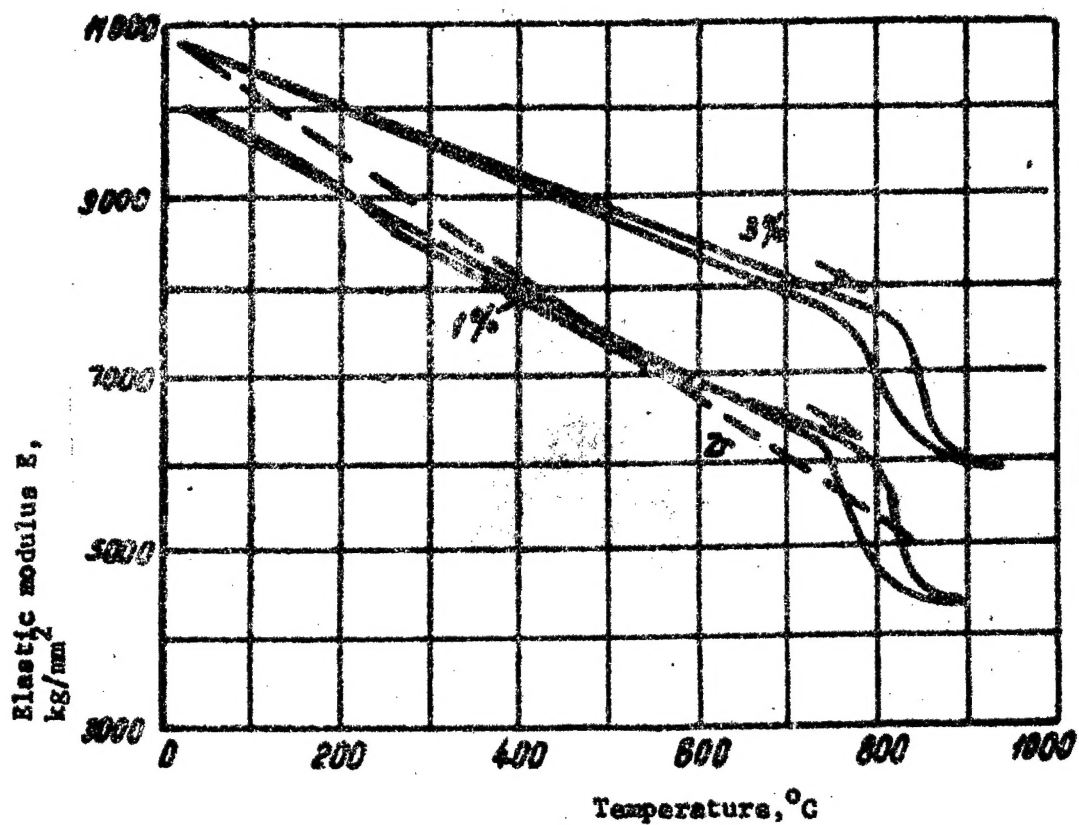| Component	Pure Zr	Sn			Al			Si		Ta
wt-%	—	2	5	10	2	3	5	1	3	25
Temperature coefficient of elastic modulus $\times 10^4$, /°C	6.4	5.9	5.5	5.2	5.2	4.6	4.6	5.2	3.7	4.85

Fig. 6. Variation of elastic modulus of
zirconium alloys with 1 and 3%
silicon during heating and cooling.

state diagram /6/.

The temperature of the $\alpha \longrightarrow \beta$ transformation, determined by thermoelastic methods for an alloy with 33% titanium, exceed by 50°C the data shown in /6/ whereas for other alloys of this system, the transformation temperatures are near to those already known.

It is interesting to note that the elasticity modulus changes with temperature at a lower rate in the β-phase range than in the α-range; this was observed both for zirconium alloys with niobium /5/ and for zirconium alloys with titanium.

Conclusions

In this work, changes in the elastic modulus of zirconium were investigated; zirconium alloys with (1) elements forming solid solutions based on α-zirconium (oxygen, tin, aluminum, titanium) (2) elements which remain fully or partially in the β-phase after hardening (niobium, molybdenum) and (3) elements forming intermetallic compounds with zirconium (silicon, aluminum), were studied. Young's modulus was measured for alloys of zirconium with niobium as well as with titanium, which form continuous series of solid solutions.

All elements forming solid solutions decrease the elastic modulus of zirconium both at room and at elevated temperatures; the elastic modulus decreases especially upon alloying with elements which, upon hardening, fix the β-phase.

Alloying with silicon, which forms intermetallic compounds and is slightly soluble in zirconium, does not noticeably influence the elastic modulus when the additions are low; however, if the content in the intermetallic phase of the alloy is adequately high, the elastic modulus increases, especially at elevated temperatures. Alloys with molybdenum hardened from the β-range and heated to 325-450°C show dissociation of the metastable β-phase. This results in a considerable increase in the elastic modulus, since during the dissociation the transitional phase is formed which has a high elastic modulus and a complex structure.

With increasing temperature, the elastic moduli of the α-solid solutions approach the elastic modulus of zirconium, while that of the alloys containing intermetallic phases exceeds the modulus of zirconium. This increase becomes greater at higher temperatures.

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